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TITLE: INDIRECT MEASUREMENTS OF HYDROGEN: THE DEFICIT METHOD
FOR A MANY-COMPONENT SYSTEM

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# INDiRECT MEASUREMENTS OF HYDROGEN: THE DEFICiT METHOD FOR A MANY-COMPONENT SYSTEM

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## ABSTRACT

We have developed a simple technique for determining hydrogen atomic fraction from the ion backscattering spectrometry (IBS) signals of the remaining species. This technique uses the surface heights of various IBS signals in the form of a linear matrix equation. We apply this technique to *in situ* analysis of ion-beam-induced densification of sol-gel zirconia thin films, where hydrogen is the most volatile species during irradiation. Attendant errors are discussed with an emphasis on stopping powers and Bragg's rule.

## INTRODUCTION

We have shown previously that sol-gel zirconia thin films can be densified via ion irradiation instead of conventional heat treatment [1]. The films undergo chemical and structural changes during irradiation which also leads to species loss. Our interest lies in determining the relative rates of species loss of these films. Through the use of an implantation chamber that allows *in situ* ion beam analysis, the densification phenomenon can be monitored with minimum variation of experimental parameters [2].

The purpose of this paper is to implement a method whereby hydrogen content in a sample containing n atomic species can be computed from the ion backscattering spectrum signal heights of the n-1 remaining species. The presence of hydrogen, a species hidden to IBS, increases the stopping power per unit hydrogen-free target atom thereby reducing signal heights of the visible species. The 'deficits' in the signal heights provide the quantitative information necessary for computing the hydrogen content.

Sol-gel zirconia thin films contain five components: zirconium, oxygen, carbon, hydrogen, and hafnium. Starting with an expression of surface signal heights for each of the four visible components and using the conservation condition, a system of five equations in five unknowns can be written which can then be solved for the atomic fraction of each component such that

$$sx = [0\ 0\ 0\ 0\ 1]^T \rightarrow x = s^{-1}[0\ 0\ 0\ 0\ 1]^T \tag{1}$$

where $s$ is a stopping power matrix conjugated with the conservation condition, $x$ is the atomic fraction matrix, such that $x_j$ is the atomic fraction of species $j$. Each element of the stopping power matrix, $s$, is given by

$$s_{ij} = \begin{cases} \left[ \varepsilon_\bullet \right]_i^j - \delta_{ij} \dfrac{Q\Omega\mathscr{E}}{\cos\theta_1}\,\sigma_i\!\left(E_\bullet\right) \Big/ H_j & \text{if } i \leq 4, \\[2mm] 1 & i = 5. \end{cases} \qquad (2)$$

where $\left[\varepsilon_\bullet\right]_i^j$ is the stopping power factor taken in the surface energy approximation for scattering from species $i$ [3] and stopping in species $j$, $\delta_{ij}$ is the Kronecker delta function, $Q$ is the total number of incident particles, $\Omega$ is the detector solid angle, $\mathscr{E}$ is the channel-to-energy conversion factor, $\theta_1$ is the entrance angle of the incident beam with respect to the surface normal, $\sigma_i(E_\bullet)$ is the scattering cross-section from species $i$ evaluated at the incident energy, $E_\bullet$, and $H_j$ is the IBS signal surface height of species $j$. Since hydrogen is not measurable by IBS then its corresponding height equation is replaced by the conservation condition, $\Sigma\, x_j = 1$.

As the sample spectrum consists of four isolated peaks, the areal density of each visible species as calculated from the peak area, could be used to reduce the above set of equations to five linearly dependent equations in one unknown, the atomic fraction of hydrogen. However only the heights are used here to illustrate the extension of the method to thicker targets, the depths of which are not probable by the analysis beam.

The uncertainty in a function $f$ can be calculated by varying each experimental parameter $x_i$ by its uncertainity $\sigma_i$ and summing in quadrature over all parameters according to the following approximation:

$$\sigma^2 = \sum_i \left( \frac{f\left(x_i + \sigma_i\right) - f\left(x_i - \sigma_i\right)}{2} \right)^2 \qquad (3)$$

Note that $\sigma^2$ in this context is the variance of the function $f$ not the scattering cross-section used in Eq. (2).

An often overlooked component of uncertainty is not included in Eq. (3), and as such requires special attention. The accuracy of Bragg's rule predictions of stopping power in a multi-element target is an issue that has been thoroughly summarized [4]. As the results of the test of Bragg's rule are usually in the form of fractional deviations from the prediction, we promulgate this idea by scaling its prediction by the same amount. A summary of relevant literature suggests that 5% is a prudent figure for a typical deviation.

## EXPERIMENTAL

A film of sol-gel zirconia was deposited onto a [100]-oriented silicon wafer. A two cm square piece of that wafer was installed into the end station of a 200 kV implanter with an interconnected 3 MV analysis accelerator as described elsewhere [2].

The methodology outlined in Eqs. (1) and (2) was implemented in MATHCAD using stopping power data from TRIM. The method was tested against theoretical simulations from RUMP and direct measurements using forward recoil energy spectrometry (FRES). The height of the silicon substrate signal was used as a measure of the total integrated charge-solid angle product.

Uncertainty in the computed hydrogen atomic fraction was computed using appropriate uncertainties for each experimental parameter according to Eq. (3). For comparison, the contributions that are associated with random uncertainties, i.e. variations in beam energy, signal heights, and scattering geometry, were distinguished from those of stopping powers and Bragg's rule predictions. The uncertainty in stopping powers was estimated from the anthology of data assembled by Ziegler [5]. Potential deviations in Bragg's rule were incorporated by decreasing all stopping powers by 5% and summing the effect on hydrogen atomic fraction in quadrature as per Eq. (3).

## RESULTS/DISCUSSION

The signal heights of a RUMP simulation of an IBS spectrum were used in Eq. (1) above, and the computed hydrogen fraction was different by 6% than that simulated. Further, results of IBS and FRES spectra were compared and the hydrogen atomic fractions calculated were different by 29%, which can be primarily attributed to uncertainties in stopping powers.

Representative IBS spectra collected during an implantation/analysis sequence are shown in Fig. 1 to illustrate the change of the spectra with ion dose. From high to low energy, the peaks of hafnium, zirconium, oxygen, and carbon can be seen, as indicated by the surface energy markers. The most obvious change with dose is the increase in the height of the zirconium peak. Not readily evident is the decrease in height of the oxygen and carbon peaks and increase in height of the hafnium peak. These changes result from the loss of oxygen, carbon, and hydrogen from the film during irradiation. The area of the zirconium peak and thus the amount of zirconium present remained ostensibly constant through all experiments.
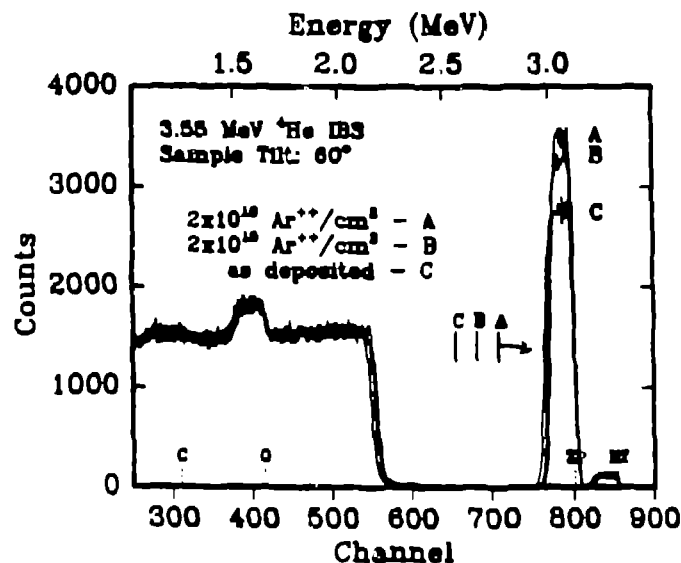


Figure 1. IBS spectra of Ar implanted sol-gel zirconia on a Si substrate. Surface markers are given for Hf, Zr, O, and C.

Twelve IBS spectra, some of which are shown in Fig. 1, were processed according to Eq. (1) and the hydrogen atomic fraction remaining in the film is given in Figs. 2a and b. Fig. 2a depicts the results on a linear plot whereas Fig. 2b shows the same data replotted with a logarithmic abscissa. In both cases a clear trend is seen as hydrogen leaves the film. The error bars in Fig. 2a represent contributions from random uncertainties. The

error bars in Fig. 2b however, represent the absolute uncertainty in the computed hydrogen atomic fraction.

The conclusion from comparison of the two sets of error bars is that this technique of computing hydrogen atomic fraction is precise but not accurate. It is particularly applicable to systems, such as ion-beam-induced densification of sol-gel zirconia thin films, where the rate of hydrogen loss is of interest, with little concern for the absolute value of composition. Indeed the majority of the inaccuracy stems from the effect of the unknown stopping power of each species of the target and the potential deviations in Bragg's rule.
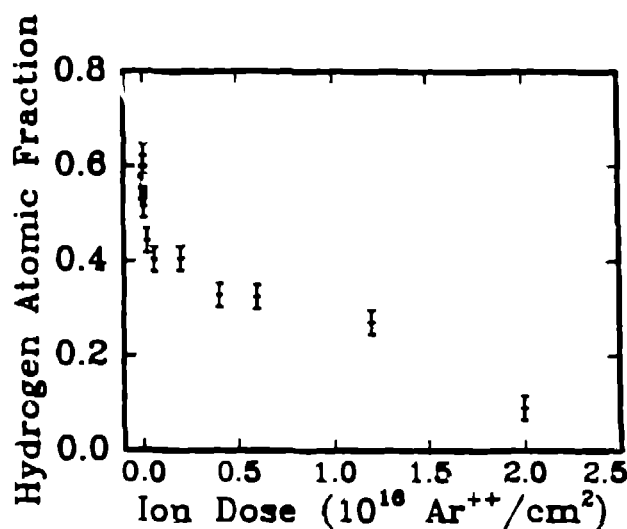


Figure 2a. The atomic fraction of hydrogen versus Ar dose. Error bars represent random uncertainty.
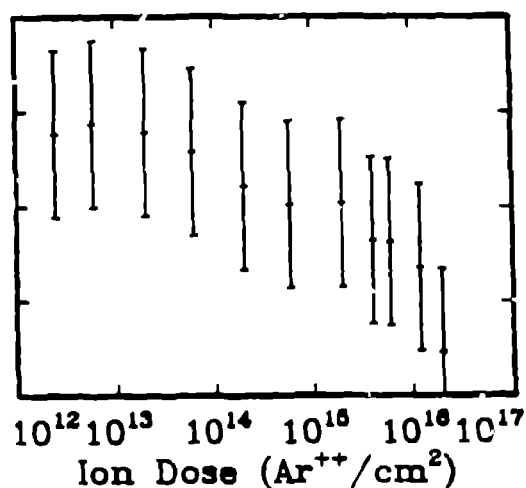
Figure 2b. The same data as in Fig. 2a replotted on a semi-log plot. The error bars represent absolute uncertainty.

## CONCLUDING REMARKS

We have developed a simple method for computation of hydrogen content in thick films using only IBS signal heights. The method has been demonstrated for a system where the rate of hydrogen loss is of more interest than the absolute value of composition. The largest contributors to the absolute uncertainty of the computed hydrogen atomic fraction are the uncertainties in the stopping powers and the potential deviation in Bragg's rule predictions. This work was sponsored by the Army Research Office (R. Reeber, Contract No. DAAL03-89-K-0154). Acknowledgments are due to Caleb Evans and Mark Hollander of the Ion Beam Materials Laboratory at Los Alamos National Laboratory. This work supported in part by the U.S. Dept. of Energy.

## REFERENCES

1. T. E. Levine,et al., J. Am. Ceram. Soc. 76, 1369 (1993).
2. Ning Yu et al., Nucl. Instrum. Meth. B, in press.
3. W.K. Chu et al. , in: Backscattering Spectrometry, (Ac. Press, London, 1978) p. 82.
4. D.I. Thwaites, Nucl. Inst. Meth. B27 (1987) 293.
5. J.F. Ziegler et al. , in: The Stopping and Range of Ions in Solids, (Pergamon Press, New York, 1985).